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Colloquium: Reaction Kinetics

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Abstract

Petroleum derived gasoline is the most widely-used transportation fuel for light-duty vehicles. In order to better understand gasoline combustion, this study investigated the ignition propensity of two alkane-rich FACE (Fuels for Advanced Combustion Engines) gasoline test fuels and their corresponding PRF (primary reference fuel) blend in fundamental combustion experiments. Shock tube ignition delay times were measured in two separate facilities at pressures of 10, 20, and 40 bar, temperatures from 715 to 1500 K, and two equivalence ratios. Rapid compression machine ignition delay times were measured for fuel/air mixtures at pressures of 20 and 40 bar, temperatures from 632 to 745 K, and two equivalence ratios. Detailed hydrocarbon analysis was also performed on the FACE gasoline fuels, and the results were used to formulate multi-component gasoline surrogate mixtures. Detailed chemical kinetic modeling results are presented herein to provide insights into the relevance of utilizing PRF and multi-component surrogate mixtures to reproduce the ignition behavior of the alkane-rich FACE gasoline fuels. The two FACE gasoline fuels and their corresponding PRF mixture displayed similar ignition behavior at intermediate and high temperatures, but differences were observed at low temperatures. These trends were mimicked by corresponding surrogate mixture models, except for the amount of heat release in the first stage of a two-stage ignition events, when observed.

Keywords

Gasoline, combustion, chemical kinetics modeling, surrogate fuels, ignition

Introduction

Gasoline is the most widely used automotive fuel, so high efficiency advanced combustion engine (ACE) technologies are needed to reduce its consumption and pollutant emissions. Notable ACE technologies include homogeneous charge compression ignition (HCCI), reactivity controlled compression ignition (RCCI), premixed charged compression ignition

(PCCI), etc. In these ACEs, ignition is primarily controlled by chemical kinetics making it imperative to develop simulation tools that accurately predict the gasoline ignition behavior under engine relevant conditions.

Developing chemical kinetic models to predict gasoline ignition is complicated due to its complex molecular composition. Gasoline is composed of hundreds of hydrocarbons, making it intractable to develop chemical kinetics models containing many fuel constituents. Surrogate fuels are one promising way to model chemical kinetics of real transportation fuels. Surrogate fuels are a mixture of a small number of hydrocarbons that emulate combustion characteristics of the target transportation fuel, which could include H/C ratio, autoignition characteristics, laminar flame speeds, engine ignition phasing, pollutant emissions, etc. [1]. For gasoline spark ignition (SI) engines, the ASTM measurements of research octane number (RON) and motor octane number (MON), which reflect the ignition propensity, are two potential targets.

The need for chemical kinetic models to predict gasoline ignition has motivated experimental and theoretical studies to investigate and compare the kinetics of gasoline [2-6] with those of proposed surrogates [2,3,7-11]. Proposed surrogates have been formulated to match the H/C ratio, RON, MON, and ignition delays of target gasoline fuels. In this study, ignition delay times are measured for two non-oxygenated alkane-rich FACE (Fuels for Advanced Combustion Engines) gasoline fuels, supplied by Conoco Philips Chemical Company, and a PRF 84 blend consisting of 16 vol_{liq}% *n*-heptane and 84 vol_{liq}% 2,2,4-trimethylpentane (*iso*-octane). The two FACE gasoline fuels, FACE A and FACE C, are chosen because they have nearly identical H/C ratio, RON (~84), MON (~84), and zero sensitivity (S=RON–MON). Binary blends of *n*-heptane and *iso*-octane, referred to as primary reference fuels (PRFs), are conventionally used as gasoline surrogates; hence, a PRF 84 surrogate is chosen for experimental testing, as its RON and MON are 84 by definition. The three test fuels

investigated herein provide a basis to examine whether fuel blends with identical RON and MON exhibit similar ignition response in fundamental combustion systems, i.e., shock tubes (ST) and rapid compression machines (RCM), under engine-relevant conditions. Furthermore, multi-component surrogates for FACE A and C gasoline fuels are formulated based on results from a detailed hydrocarbon analysis (DHA), and a chemical kinetic model is developed for those surrogates to compare with the measurements of ignition delay times for FACE A, FACE C, and PRF 84.

Methodologies

Detailed hydrocarbon analysis

The compositions of FACE A and C fuels were determined using DHA at Saudi Aramco's Research and Development Center, in accordance with the standard test method ASTM D6733 and D6730. The standard DHA provides the major hydrocarbon groups in the gasoline sample, such as *n*-paraffins (*n*-alkanes), i*so*-paraffins (*iso*-alkanes), olefins (alkenes), naphthenes (cycloalkanes), and aromatics (PIONA), along with their vol%, wt%, and mol%. The method was extended for complete isomer resolution of all species in the gasoline sample, such that various *iso*-alkanes, alkenes, cycloalkanes, and aromatics of the same carbon number were distinguishable. The complete DHA report is provided as supplementary material.

FACE fuel surrogate formulation and kinetic modeling

Based on the FACE gasoline specifications and the DHA results, binary and multi-component surrogates are proposed to match the ignition characteristics of FACE A and FACE C fuels. Attention is devoted to the selection of a suitable palette of compounds that represent the FACE fuels' primary components. The DHA results (Table 1, Figure **S**1, and supplementary analytical reports) reveal that FACE A fuel contains mainly *iso*-alkanes (84 mol%) with the remainder being 13 mol% *n*-alkanes and 2 mol% cyclo-alkanes. FACE C fuel contains 65

mol% *iso*-alkanes, 29 mol% *n*-alkanes, and 4 mol% aromatics. The present DHA results also include complete resolution of each constituent's carbon number and isomer. FACE A and C fuels are comprised of large fractions of C_4-C_6 *n*-alkanes and *iso*-alkanes. The higher molecular weight *iso*-alkanes are primarily isomers C_7 and C_8 mono-, di-, and tri-methylalkanes. Both the blends have similar amounts of di- and tri-methylalkanes, while the major differences in composition are in the fractions of *n*-alkanes and mono-methylalkanes. A fundamental explanation on the effects of differing *n*-alkane and mono-methylalkane fractions on ignition propensity of FACE A and FACE C fuel cannot be presented because a complete understanding of methyl branch location and chain length effects on low temperature ignition is not yet available in the literature, despite notable efforts in this area [12-15].

Based on the DHA results and the suite of available LLNL chemical kinetic models [15,16], a surrogate kinetic model with the following components (Figure **1**a) is proposed to represent different classes of compounds: *iso*-alkanes – *iso*-pentane, 2-methylhexane, 2,2,4-trimethylpentane (*iso*-octane); *n*-alkanes – *n*-butane and *n*-heptane; and aromatics – toluene. *Iso*-octane, *n*-heptane, and toluene are the three components commonly adopted for gasoline surrogate formulations, and validated kinetic mechanisms are available to simulate their mixtures. Beside these three main components, two *iso*-alkanes (*iso*-pentane and 2-methylhexane) and a short chain-alkane (*n*-butane) have been added to the proposed fuel palette. These additions allowed us to reproduce the content of components present in high concentration (e.g, *iso*-pentane), as well as the average chain length of the *n*-alkane fraction and the degree of branching in *iso*-alkanes. The chemical kinetic model for the aforementioned components was developed by merging the 2-methylhexane kinetic model proposed by Sarathy et al. [15] with the gasoline surrogates model proposed by Mehl et al. [16].

These components are finally "numerically blended" to closely match the DHA results and the octane numbers for the FACE fuels using the approach described by Mehl et al. [7], wherein the homogeneous gas-phase ignition delay time (near 25 bar and 825 K) and the slope of the NTC region across a temperature range characteristic of engine operation are correlated respectively to the anti-knock index, AKI=(RON+MON)/2, and the sensitivity, S=RON–MON. The three test fuels are modeled as follows: PRF 84 ~ 17.6 mol% *n*-heptane and 82.4 mol% *iso*-octane; FACE A_{surr} ~ 7 mol% *n*-butane, 15 mol% *iso*-pentane, 11 mol% 2-methylhexane, 7 mol% *n*-heptane, and 60 mol% *iso*-octane; and FACE C_{surr} ~ 17 mol% *n*-butane, 8 mol% *iso*-pentane, 5 mol% 2-methylhexane, 11 mol% *n*-heptane, 3 mol% toluene, and 51 mol% *iso*-octane. The resulting PIONA compositions, projected RON and MON, and H/C ratios (listed in Table 1) indicate that the surrogates match these target real fuel properties. Furthermore, real FACE fuel average molecular weight is matched better with the multi-component surrogates when compared to PRF 84, due to the addition of low molecular weight *n*- and *iso*-alkanes in the former. Thus, we expect that the proposed multi-component surrogates would better reproduce laminar flame speeds, emissions, and spray combustion of the real fuels. All ignition delay simulations were conducted in CHEMKIN PRO [17] using the homogeneous batch reactor module including relevant facility effects.

Low-pressure shock tube

High-temperature ignition delay time measurements were performed in the Low-Pressure Shock Tube (LPST) facility at KAUST. The shock tube is constructed from stainless steel and the inner surface is electropolished to reduce boundary layer effects. The shock tube has an inner diameter of 14.2 cm, driven section of 9 meter length, and the length of the driver section can be varied (maximum 9 meter) depending on the required test times. This device has been previously described in detail [18]. The shock tube is heated uniformly to 348 K for these experiments. Ignition delay times were measured behind reflected shock waves over the temperature range of 1100 K to 1500 K, nominal pressures of 10 bar, and equivalence ratios

of 0.5 and 1 with argon as the diluent. Ignition was determined using the pressure history and OH* chemiluminescence near 306 nm. The ignition delay time is defined as the time interval between the arrival of the reflected shockwave and the onset of ignition, determined by extrapolating the steepest rise in both pressure and OH* chemiluminescence to the respective pre-ignition zero signal. In all experiments, the fuel concentration is fixed at 0.4%. The estimated uncertainty in ignition delay times is ±17% owing mainly to the uncertainty in reflected shock temperature. The LPST ignition delay is modeled with an imposed volume history to account for the experimentally measured pressure gradient, dP/dt=3% per millisecond.

High-pressure shock tube

Measurements of ignition delay times spanning low, intermediate, and high temperatures were carried out in a heated high-pressure shock tube (HPST) at Rensselaer Polytechnic Institute using the reflected shock technique. This shock tube has been described by Wang and Oehlschlaeger [19] and references therein, hence, only details relating to the present study are provided here. Ignition delay times were measured for fuel/air mixtures at equivalence ratios of 0.5 and 1.0, temperatures ranging from 714 to 1262 K, and nominal pressures of 20 and 40 bar. The ignition event was measured by monitoring the pressure history, and the ignition delay time has the same definition as in the LPST. Following the passage of the reflected shock wave, the pressure was observed to slowly rise due to viscous gas dynamics at a rate of dP/dt=2–3% per millisecond, which is incorporated into kinetic modeling simulations. The uncertainty in ignition delay is ±20% (95% confidence interval), where the majority of ignition delay uncertainty stems from uncertainty in the reflected shock temperature.

Rapid compression machine

The University of Connecticut RCM used in the current study employs a pneumatically driven creviced piston. The pneumatically driven piston is brought to rest towards the end of compression hydraulically. Compression is a single stroke event with compression time of about 30 ms. Dynamic pressure in the reaction cylinder is measured using a thermal shock resistant Kistler 6125C pressure transducer along with a 5010B charge amplifier. Compressed conditions, i.e., pressure and temperature in the reaction cylinder at the end of compression, can be varied independently in the current experiments by changing initial charge pressure, pre-heat temperature, and compression ratio. Compression ratio can be changed by adjusting the clearance length and stroke length independently. Homogeneous fuel/air mixtures, the test charge for experiments, are prepared separately in a stainless steel chamber. All the RCM experiments were conducted with a preheat of 333 K. Further details of the experimental facility can be found in [20]. Ignition delay times are measured for fuel/air mixtures at equivalence ratios of 0.5 and 1.0, temperatures ranging from 632 to 745 K, and nominal pressures of 20 and 40 bar. Ignition delays, both first stage ignition delay (when observed) and total ignition delay, are defined as the time difference between the end of compression and the local maxima of pressure derivative for the corresponding ignition event. For each experimental data point reported a minimum of five repeated runs are performed and the value closest to the mean is reported. The ratio of the standard deviation to the mean of the ignition delays is less than 10% for all the data points reported.The typical scatter in the measured ignition delays is within 10% of the reported value. The RCM ignition delay is modeled with an imposed volume history to account for the compression stroke and the heat loss after compression, as described by Mittal and Sung [21].

Results and Discussion

LPST ignition delays

Figure **1**b presents the shock tube ignition measurements for FACE A, FACE C, and PRF 84 from the LPST. At constant fuel concentration, all fuels display high temperature Arrhenius

behavior and decreasing ignition delay times with decreasing equivalence ratio. Under these high-temperature conditions, the three fuels display indistinguishable ignition delay at both equivalence ratios and across the range of temperatures. The proposed chemical kinetic models for FACE A, FACE C, and PRF 84 quantitatively over predict the measured ignition delay times. This discrepancy was investigated and is attributed principally to the rate of *iso*-butene consumption. At these high-temperature conditions, *iso*-octane is the primary component in all surrogate formulations and decomposes primarily to *iso*-butene. Increasing the rate of *iso*-butene consumption decreases ignition delay times; interrogation of this underlying chemistry is being pursued but is beyond the scope of the present work. The models are able to reproduce the qualitative experimental trends, most notably the minimal differences in ignition delay of FACE A, FACE C, and PRF 84. These features are discussed in more detail later.

HPST ignition delays

Figure **1**c-f presents the shock tube ignition data from the HPST. The data displays negative temperature coefficient behavior followed by high-temperature Arrhenius behavior. For these fuel-air mixtures, ignition delay times decrease with increasing equivalence ratio across all temperature and pressure conditions studied. For increasing pressures from 20 to 40 bar, the ignition delay times decreases by approximately a factor of 2 at low and intermediate temperatures (below 1000 K) and about a factor 1.5 at higher temperatures. FACE A, FACE C, and PRF 84 exhibit indistinguishable ignition delay times at nearly all temperatures, mixture fractions, and pressures studied. Along with the aforementioned LPST results, this suggests that a PRF 84 surrogate captures the ignition propensity of the standard gasoline test fuels at most conditions. An exception to this consistency is observed at the very lowest temperatures studied (i.e., below 740 K) at 20 bar and stoichiometric fuel/air mixtures. At these conditions, the FACE gasoline fuels exhibit measurably longer ignition delay times than the PRF 84 fuel (30-40% longer).

Ignition delay time predictions of the detailed chemical kinetic model for FACE A and FACE C surrogates and PRF 84 are also shown in Figure **1**c-f. The model well captures the experimentally observed effects of temperature, pressure, and equivalence ratio on ignition delay time. However, there is approximately a factor of 1.5 to 2 quantitative disagreement between the model predictions and experiments at low and intermediate temperatures. At these conditions, the model is generally less reactive than experiments. The model predictions improve with increasing temperature and pressure and decreasing equivalence ratio. Again, the surrogate modeling simulations reproduce the trend of indistinguishable reactivity amongst FACE A, FACE C, and PRF 84 observed in all but the lowest temperature HPST experiments.

RCM ignition delays

RCM ignition delay measurements at 20 bar and 40 bar for two equivalence ratios investigated are shown Figure **1**c-f. The temperatures covered in the RCM experiments are notably lower (632–745 K) than those studied in the shock tubes, and hence complement the shock tube data. At 20 bar stoichiometric condition, the lowest temperature shock tube experiments coincide with the highest temperature RCM experiments; at this condition (~740 K) there is good agreement in the ignition delay measurements obtained from the two devices. The effects of temperature, pressure, and equivalence ratio on ignition delay times of FACE A, FACE C, and PRF 84 are similar to that observed in the shock tube, wherein increasing any of these parameters causes a decrease in ignition delay time. It is observed that FACE A and FACE C exhibit similar ignition delay times in the RCM, both of which are 25-40% less reactive than PRF 84, consistent with the lowest temperature HPST results.

Modeling predictions for PRF 84 and FACE A and C surrogates for RCM conditions are also shown in Figure **1**c-f. The simulations well predict ignition delay at 20 bar but over predict

ignition delay at 40 bar by ~50%. The qualitative trend of increased reactivity for PRF 84 relative to FACE A and C is well reproduced by the simulations. Figure **2**a-b present RCM pressure histories at 20 bar, stoichiometric fuel/air mixtures, and two different temperatures. At 658 K, all three tested fuels display single-stage ignition, with ignition delay times increasing in the order of PRF 84 < FACE A ≤ FACE C. Simulations are able to reproduce the observed single-stage ignition and ordering of fuels with high accuracy. At higher temperatures (e.g., 727 K), the fuels display two-stage ignition behavior with less prominent differences between the three fuels. The simulations for all three fuels at these conditions over predict the first-stage and total ignition delay times. Furthermore, the simulations exhibit higher pressures after first-stage ignition when compared to the experiments.

Kinetic modeling analysis

The present experimental and kinetic modeling results indicate that FACE A, FACE C, and PRF 84 exhibit nearly indistinguishable ignition delay times at high temperatures (i.e., above 800 K). These results are consistent with those presented by Dooley et al. [22], where a surrogate mixture without all the distinct chemical functionalities present in the real fuel successfully reproduced its high-temperature combustion behavior. Dooley's work demonstrated how a surrogate composition that emulates the development of the active radical pool is sufficient to reproduce shock tube ignition data, as this controls the combustion kinetics phenomenon. In our study, the PRF 84 surrogate well reproduces the active radical pool at high temperatures, and is thus acceptable for matching the reactivity of FACE A and C.

At lower temperatures (i.e., 630–750 K), both experiments and modeling results indicate that PRF 84 is more reactive than FACE A and C. Low-temperature fuel reactivity is controlled by the relative importance of low-temperature chain branching, chain propagating, and chain terminating reactions. The importance of these reaction pathways varies greatly with chemical

functionality and carbon chain length. A kinetic model sensitivity analysis of total ignition delay time to changes in reaction rate coefficients is presented in Figure **3**a-b, helping to understand the impacts of fuel surrogate formulation on high- and low-temperature reactivity. The analysis is performed under constant volume adiabatic simulations at 20 bar, stoichiometric fuel/air mixtures, and temperatures of 1050 K (Figure **3**a) and 650 K (Figure **3**b). The relative sensitivity (S_{rel}) is defined as $S_{rel} = \ln(\tau_2 / \tau_1) / \ln(k_2 / k_1)$, where τ_1 is the original total ignition delay time corresponding to the unperturbed reaction rate constant k_1, and τ_2 is the total ignition delay time corresponding to a doubling of the forward and reverse rate constants (i.e., $k_2=2k_1$). This definition results in negative sensitivity coefficients for reactions that decrease ignition delay times.

At 1050 K (Figure **3**a), the important reactions controlling the ignition of FACE A, FACE C, and PRF 84 are identical. The decomposition of H_2O_2 to OH radicals is the primary ignition-promoting reaction, followed by other radical producing reactions. H_2O_2 that does not decompose to two OH radical can react with O_2 to form two HO_2 radicals. This is another important chain branching ignition-promoting reaction at 1050 K. Chain propagating and chain branching reactions consuming CH_3 and HO_2 radicals exhibit negative sensitivities, and thus promote ignition; however, chain terminating reactions (i.e., recombination reactions) or those producing less reactive radicals exhibit positive sensitivities. It is interesting to note that H-atom abstractions from *iso*-octane by HO_2 radicals and unimolecular decomposition of *iso*-octane to produce CH_3 radicals are the only fuel-specific reactions appearing amongst the most sensitive reactions. This is attributed to the fact that the three surrogate formulations contain large fractions of *iso*-octane, and thus their high temperature reactivity is driven by its overwhelming presence. At 650 K (Figure **3**b), the important reactions controlling the ignition of FACE A, FACE C, and PRF 84 are notably different. H-atom abstraction reactions from *iso*-octane by OH radicals that lead to low temperature chain branching are important in all the surrogates. However, FACE A and C surrogates contain fractions of *n*-butane (nC_4H_{10}),

iso-pentane (*i*C_5H_{12}), and 2-methylhexane (C_7H_{16}-2), and reactions involving these molecules control low-temperature reactivity of these multi-component surrogates. H-atom abstractions from *n*-butane and *iso*-pentane inhibit reactivity because their shorter chain length and methyl substitution inhibit low temperature radical chain branching. On the other hand, H-atom abstractions from secondary C-H sites in 2-methylhexane promote reactivity because they eventually lead to low temperature chain branching [15]. Thus, the higher degree of chemical fidelity present in the multi-component surrogate mixtures compared to PRF 84 allows a better reproduction of FACE A and FACE C ignition behavior.

Conclusions

Ignition delay times for FACE A and C gasoline test fuels with a RON and MON of ~84 and a PRF 84 mixture have been measured in two shock tubes and a RCM. A DHA was performed on the gasoline fuels to determine their complex compositions. Multi-component surrogate mixtures were formulated to emulate the target real fuel composition as well as chemical and physical properties and a kinetic model was developed for those surrogates. Chemical kinetic modeling simulations were performed for PRF 84, FACE A_{surr}, and FACE C_{surr} and compared with the measured ignition delay times. At intermediate and high temperatures, the three fuels exhibit similar ignition delay times despite their differences in molecular composition. However, it was observed that PRF 84 is more reactive than the FACE fuels at low temperatures and high pressures in both the HPST and RCM. In the RCM, the experiments showed single- and two-stage behavior that was also predicted by the model, although the magnitude of the first stage heat release was over predicted. The simulations were able to qualitatively reproduce experimentally observed differences in the fuels, but quantitative differences were observed in the NTC and high temperature regions. Nevertheless, the simulations enabled an investigation into the role of fuel molecular composition on ignition behavior, and the kinetic model can be further refined to improve predictive capabilities.

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Table 1. Properties of FACE gasoline fuels and their surrogate mixtures

	FACE A	**FACE C**	**PRF 84**	**FACE $A_{surrogate}$**	**FACE $C_{surrogate}$**
RON	83.5	84.7	84	84	84
MON	83.6	83.6	84	84	84
Sensitivity	-0.1	1.1	0	0	0
H/C ratio	2.29	2.27	2.26	2.29	2.28
Avg. mol. wt.	97.8	97.2	112.0	101.5	98.4
Hydrocarbon Type, liquid mol%[1]					
n-alkanes	13.2	28.6	17.6	14.0	28.0
iso-alkanes	83.7	65.1	82.4	86.0	69.0
Aromatics	0.3	4.4	0.0	0.0	3.0
Alkenes	0.4	0.4	0.0	0.0	0.0
Cycloalkanes	2.4	1.5	0.0	0.0	0.0

[1] Determined by DHA (ASTM D6733 and D6730)

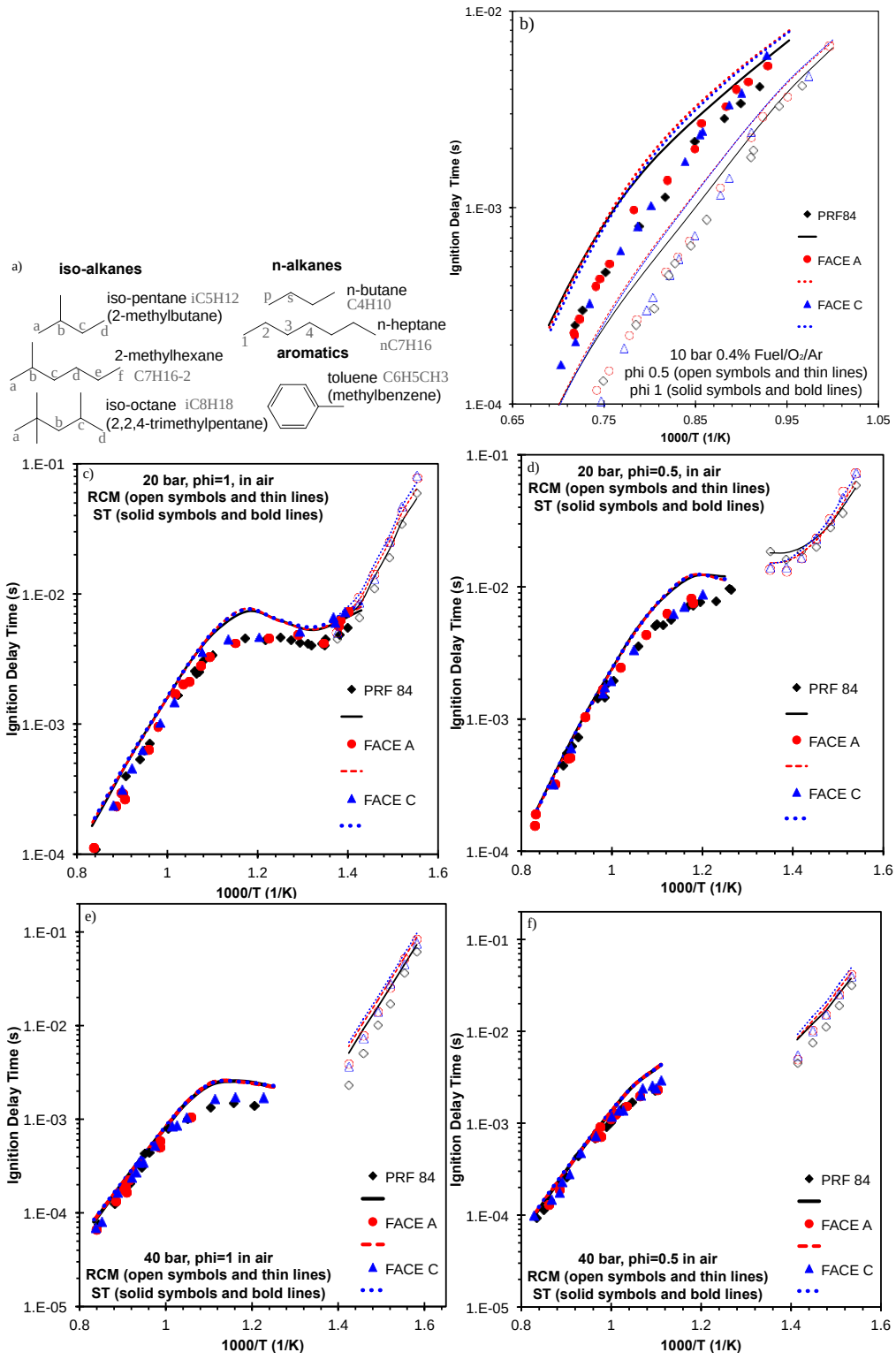

Figure 1 – a) Surrogate molecules used for FACE A and FACE C gasolines with chemical nomenclatures. Experimental data (symbols) and simulations (lines) for ignition delays in b) LPST, 10 bar, lean and stoichiometric, c) HPST and RCM, 20 bar, stoichiometric d) HPST and RCM, 20 bar, lean, e) HPST and RCM, 40 bar, stoichiometric, f) HPST and RCM, 40 bar, lean.

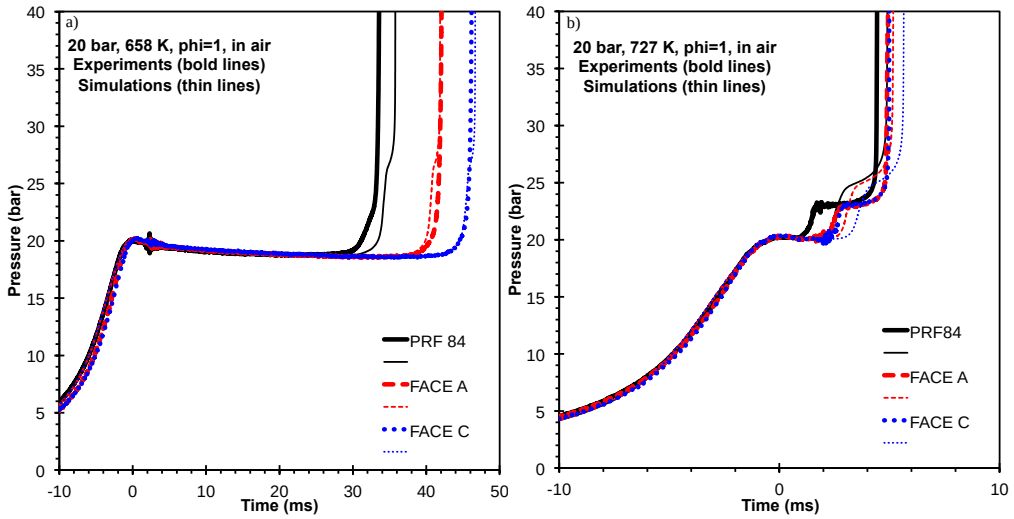

Figure 2 – Experimental (bold lines) and simulated (thin lines) pressure profiles in an RCM for stoichiometric fuel/air mixtures at a) 20 bar and 658 K and b) 20 bar and 727 K.

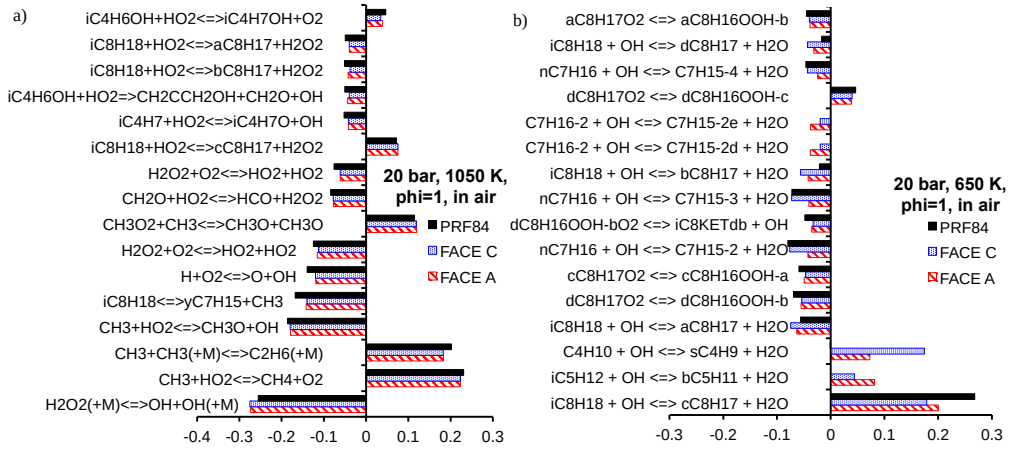

Figure 3 – Sensitivity of the total ignition delay time to changes in the reaction rate coefficients for the surrogate models of PRF 84, FACE A, and FACE C. Initial conditions for constant-volume adiabatic simulations are 20 bar, stoichiometric fuel/air mixtures, and a) 1050 K and b) 650 K.

Supplementary Materials

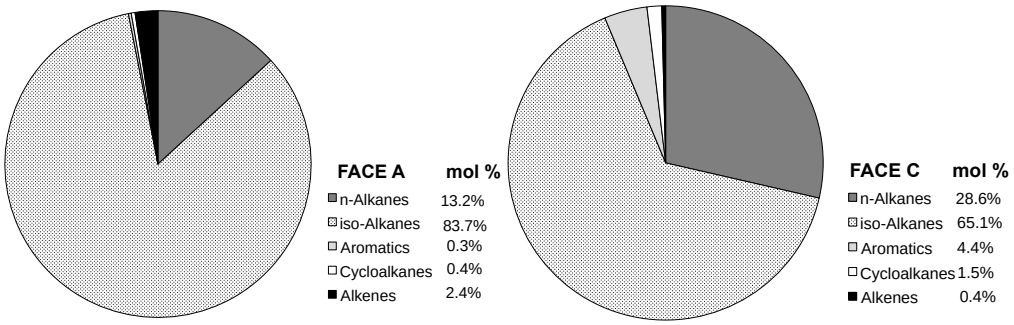

Figure S1 - PIONA analysis of FACE A (left) and FACE C (right) gasoline test fuels utilizing detailed hydrocarbon analysis (DHA)